Translated from *Uspekhi Khimii*, **43**, 519-536 (1974) U.D.C. 541.64 : 547.308 : 547.311.2

Polymerisation of αβ-Unsaturated Sulphur-containing Compounds

A.V.Sviridova and E.N.Prilezhaeva

The review deals with the present state of the problem of the polymerisation of unsaturated sulphur-containing monomers with sulphide, sulphoxide, and sulphone groups in the immediate vicinity of the double bond. The mechanisms of polymerisation reactions involving various catalytic systems and the effect of the heteroatom on the polymerisation of the above monomers as well as the fields of practical application of the polymers based on them are discussed.
The bibliography includes 167 references.

CONTENTS

I. Introduction 200
II. Polymerisation and copolymerisation of vinyl monomers containing bivalent sulphur 200
1. Polymerisation of vinyl sulphides, divinylmercaptals, and divinylmercaptols
2. Polymerisation of vinyl thioloacylates
III. Polymerisation and copolymerisation of vinyl monomers containing oxidised sulphur 204
1. Synthesis of polymers containing sulphoxide groups
2. Polymerisation and copolymerisation of vinyl sulphones

I. INTRODUCTION

Numerous studies dealing with the polymerisation of unsaturated sulphur-containing compounds have now been published. However, these investigations have not been discussed from a single standpoint and brief reviews [1-3] on this problem in certain monographs cannot claim to cover the literature completely.

Nevertheless, examination of the polymerisation of such compounds is important from both theoretical and practical points of view. For example, many polymers with enhanced thermal stability and resistance to ozone [4], organic solvents, radiation, and ageing [5] are known to contain in sulphur atoms their structure. Moreover, the problem of the polymerisation of unsaturated sulphur-containing compounds has a direct bearing on the elucidation of the nature of the interaction between the sulphur atom and the π-electron system.

The aim of the present review was to give a general and systematic account of the available data and to draw the attention of research workers to this interesting and hitherto inadequately investigated field. The review deals with the polymerisation of unsaturated compounds with sulphur-containing functional groups in the immediate vicinity of the double bond. The polymerisation of ethylenesulphonic acids and their esters will not be considered, since a fairly complete review on this subject has already been published [4].

II. POLYMERISATION AND COPOLYMERISATION OF VINYL MONOMERS CONTAINING BIVALENT SULPHUR

1. Polymerisation of Vinyl Sulphides, Divinylmercaptals, and Divinylmercaptols

A comprehensive study of the physical and chemical properties of unsaturated sulphides [6] led to the conclusion that, depending on the conditions, in the conjugation with neighbouring multiple carbon–carbon bonds the sulphur atom can (1) exhibit electron-donating properties—in the attack on the substrate by electrophilic reagents or in its interaction with electron-accepting groups, (2) can behave as an electron acceptor owing to the involvement of the d-orbitals, which occurs in certain systems where there is attack by powerful electron-donating reagents, and (3) can stabilise the free-radical state of the system when the latter is attacked by free radicals or subjected to excitation by light owing to the overlapping of the p_C-d_S or p_C-p_S orbitals formally imitating the C=C group.

However, it has been established [6] that, in contrast to alkylthioacetylenes, the sulphur atom does not behave as an electron acceptor in alkylthio-olefins, for example in their reaction with amines.

In accordance with the foregoing considerations, there are literature data only for cationic and free-radical polymerisation of both substituted and unsubstituted alkyl vinyl and aryl vinyl sulphides.

a. Cationic polymerisation and copolymerisation of vinyl sulphides. The polymerisation of αβ-unsaturated sulphides was described for the first time by Reppe [7-10], who employed BF_3, SO_2, and I_2 as catalysts. Later it was noted that in the presence of $AlCl_3$ or other Friedel–Crafts catalysts vinyl sulphides undergo copolymerisation with alkenes, forming rubber-like materials [11,12] suitable as additives to lubricating oils [13].

The polymerisation of vinyl sulphides under cationic conditions was investigated in greater depth by Soviet workers [14-18]. It was found that cationic catalysts such as $FeCl_3.6H_2O$ and $SnCl_2$, in the presence of which alkyl vinyl ethers [19] polymerise in high yields, are completely inert with respect to alkyl vinyl sulphides. In the presence of $BF_3.OEt_2$ or $SnCl_4$, alkyl vinyl sulphides form low-molecular-weight oligomers [15] ($M \simeq 1000-2000$). The nature of the reaction differs significantly from the polymerisation of vinyl ethers where negligible traces of $BF_3.OEt_2$ give rise to an explosive reaction. A considerable amount of the catalyst and prolonged heating are necessary for the polymerisation of vinyl sulphides.

The low reactivity of vinyl sulphides in relation to cationic catalysts can be explained on the one hand by the lower nucleophilicity of their double bond compared with vinyl ethers and on the other by the possibility of the formation via the sulphur atom of comparatively stable complexes of the donor–acceptor type [16,17].

It is believed[20] that the reason for the weaker mesomeric effect of the sulphur atom compared with the oxygen atom is its greater covalent radius (r) compared with the atomic radius (R). This gives rise to steric hindrance to the overlapping of the $p_C - p_X$ orbitals (a measure of the tendency towards such overlapping is provided by the ratio R/r, which amounts to 1.90 for oxygen and 1.54 for sulphur). However, the order of the reactivities of the sulphur-containing monomers in polymerisation,

$$CH_2{=}CHSPh > CH_2{=}CHOCH_2CH_2SCH{=}CH_2 > CH_2{=}CHSCMe_3 > CH_2{=}CHSEt > CH_2{=}CHSCH_2CH_2OBu > CH_2{=}CHOCH_2CH_2SEt > CH_2{=}CHSCH_2CH_2SEt$$

cannot be accounted for solely by the differences between the nucleophilic properties of the double bond. The observed phenomenon is related to changes in the basicity of the sulphur atom, which constitutes the second reaction centre in the molecule or, in other words, to the capacity of the catalyst for complex formation via this atom. The decrease of the effective concentration of the catalyst must constitute an additional factor reducing the rate of cationic polymerisation. Thus phenyl vinyl sulphide shows the highest reactivity in ionic polymerisation and yields a polymer in the presence of iron(III) chloride which is inert with respect to all other monomers of this series, while 2-ethylthioethyl vinyl sulphide does not polymerise even on very prolonged heating with $BF_3.OEt_2$. All attempts[21] at the polymerisation of the optically active (+)-s-butyl *o*-vinylbenzyl sulphide under the influence of cationic catalysts ($SnCl_4$, BF_3, $TiCl_4$, $FeCl_3$, $ZnCl_2$, and ZnI_2) at temperatures ranging from $-78°$ to 115°C did not lead to the desired results either. Moreover, the above compound not only does not polymerise under these conditions but actively inhibits the polymerisation of styrene. The fairly marked tendency of t-butyl vinyl sulphide towards ionic polymerisation[16] is consistent with its enhanced tendency towards hydrolysis in an acid medium and may be accounted for by the greater nucleophilicity of the double bonds and the steric hindrance to the formation of a complex with the catalyst.

Cationic copolymerisation data[17] are in full agreement with the results obtained in homopolymerisation. Thus phenyl vinyl sulphide forms copolymers with styrene in the presence of $SnCl_4$ and with butyl vinyl ether in the presence of both $SnCl_4$ and $FeCl_3.6H_2O$. On the other hand, ethyl vinyl sulphide forms on initiation by $SnCl_4$ only an insignificant amount of a copolymer with butyl vinyl ether. Styrene, which usually polymerises very readily under the influence of $SnCl_4$, not only does not enter into copolymerisation with ethyl vinyl sulphide but is itself not polymerised in its presence.

The polymers and copolymers obtained on the basis of vinyl sulphides have many valuable properties: they can be used as ion exchangers[22] and dielectrics[23,24], and some are fire resistant[25]. In the copolymerisation[26] of α-alkenes with compounds having the general formula $ArS(CH_2)_nCH = CH_2$ (where X = Ar or Alk; $n = 1-12$) under the influence of $TiCl_4$, Et_3Al, Et_2AlCl, and $Et_3Al_2Cl_3$, polymers were obtained which did not lose their elasticity at 140°C in the course of 360 h, whereas polypropylene becomes brittle after only 12 h.

In conclusion one must note that the cationic polymerisation of sulphur-containing monomers is determined to a smaller extent by the properties of the double bond and to a greater extent by the nature of the sulphur atom, since the latter behaves as a second reaction centre binding the catalyst and lowering thereby its effective concentration. In other reactions such as hydrolysis or the addition of an alcohol, occurring under the influence of hydrogen chloride which does not show a tendency to form thionium complexes, vinyl sulphide and particularly sulphur-containing vinyl ethers can exhibit a fairly high nucleophilic reactivity of the double bond.

b. Polymerisation and copolymerisation of vinyl sulphides under the influence of radical initiators. In contrast to cationic polymerisation, free-radical polymerisation of vinyl sulphides is faster than the polymerisation of their oxygen analogues. Thus under the influence of azobisisobutyronitrile (AIBN) vinyl sulphide polymerises readily[18,27,28] giving a high yield of comparatively high-molecular-weight products, while vinyl ethers form only low-molecular-weight compounds after prolonged heating[29]. Benzoyl peroxide (BP) cannot be employed as the initiator, since it adds to vinyl sulphides via the mechanism[30]

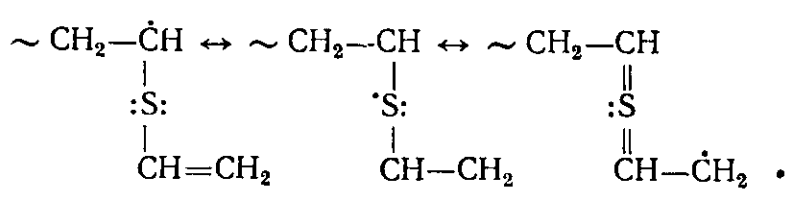
$$(PhCOO)_2 + CH_2{=}CHSEt \rightarrow PhC(O)OCH_2CH(SEt)O(O)CPh .$$

The enhanced reactivity of vinyl sulphides compared with vinyl ethers is difficult to explain without resorting to the hypothesis of the expansion of the valence shell of sulphur with employment of its *d* orbitals. The considerable contribution of the *d*-orbital interaction is indicated also by the higher value of the stabilisation factor for vinyl sulphides[31] ($Q = 0.3-0.5$) compared with vinyl ethers[32] ($Q = 0.015$).

The possibility of the stabilisation of the intermediate free radical by the involvement of the *d* orbitals of the sulphur atom was indicated for the first time by Price[33-36].

An analogous state but of a biradical type arises when unsaturated sulphide molecules are excited by light, which explains the bathochromic shifts in their ultraviolet spectra[36].

The breakdown of coplanarity is of course found to entail a decrease of the resonance stabilisation of the radical[36]. Thus, in the copolymerisation of pentachlorophenyl vinyl sulphide initiated by AIBN, Holly[37,38] obtained $Q = 0.23$, whilst for phenyl vinyl sulphide[35] $Q = 0.32$. The decrease of Q for pentachlorophenyl vinyl sulphide is due to the *ortho*-effect of the chlorine atoms, resulting in a breakdown of coplanarity. The high value of the factor Q (0.6 ± 0.1) for divinyl sulphide[33] can be explained by the possibility of the additional resonance stabilisation of the intermediate radical:



The negative values of the polar factors found from the constants for the copolymerisation of vinyl sulphides with other monomers[33] correspond to the electron-donating effect of the sulphide group, which increases the electron density of the double bond. This behaviour of the sulphide group was also concerned in the copolymerisation of ethyl vinyl sulphide with styrene and methyl methacrylate[39].

As expected, the presence of electron-accepting substituents in the vinyl sulphide molecule leads to a diminution of the electron-donating properties of the sulphur atom, expressed by the mesomeric or inductive effect, in relation to the radical or the double bond. For example, $e = -1.1$ for divinyl sulphide[33], while for methyl vinyl sulphide[34] $e = -1.35$.

A study of the polymerisation of *para*-substituted phenyl vinyl sulphides[40] established that the reactivity of the monomers in relation to the polymeric radical is directly related to the σ constants of the substituents. A similar tendency was observed also in the copolymerisation of such monomers with one another. It was found that their reactivity depends markedly only on the polar effect of the substituent, while in the polymerisation of substituted styrenes[41] the polar and resonance effects play equally important roles. The fairly high values of Q (Table 1) yet again indicate the possibility of the 3*d* orbital interaction of the sulphur atom with an adjacent radical centre.

Table 1. Copolymerisation of *p*-substituted phenyl vinyl sulphides (M_2) with styrene (M_1) and methyl methacrylate (M_1) at 60°C.

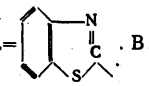
M_1	*p*-Substituent in M_2	r_1	r_2	Q	e
Styrene	MeO	3.98	0.18	0.35	−1.40
	Me	3.65	0.25	0.35	−1.10
	H	3.88	0.36	—	—
	Cl	3.57	0.32	—	—
	Br	3.42	0.31	—	—
Methyl methacrylate	MeO	0.77	0.04	0.46	−1.47
	Me	0.81	0.07	0.47	−1.29
	H	0.85	0.08	0.45	−1.26
	Cl	0.89	0.08	0.45	−1.24
	Br	0.85	0.20	—	—

Vinyl sulphides not only readily polymerise under free-radical conditions but they also copolymerise vigorously with other monomers[39,42-49]. The reactivities of the radicals derived from various monomers in relation to vinyl sulphides decrease in the sequence vinylcaprolactam[50] > methyl acrylate > methyl methacrylate > styrene, which is consistent with the reactivities of these radicals in relation to other monomers described in the literature[51].

It has been noted that any mixtures of ethyl vinyl sulphide with butyl vinyl ether in the presence of AIBN yield copolymers greatly enriched in ethyl vinyl sulphide units. Data for the compositions of the copolymers obtained from these monomers and methyl methacrylate show that in this case the sulphide monomers are more reactive than their oxygen analogues. Whereas the copolymers of vinyl ethers with the majority of monomers (for any composition of the initial mixture) contain as a rule not more than 50 mole % of vinyl units, vinyl sulphides can yield copolymers with a very high content of sulphide units. For example, in the copolymerisation of bis-(4-vinylphenyl)-sulphide (M_2) with styrene (M_1) the following monomer reaction factors were obtained[52]: $r_1 = 0.60$; $r_2 = 1.50$.

The reactivities of alkyl vinyl sulphides $AlkSCH{=}CH_2$ (M_2), where Alk = Me, Et, i-Pr, n-Bu, i-Bu, t-Bu, $PhCH_2$, and Ph, and of ethyl vinyl ether (M_3) in relation to various polymeric radicals M_1 (styrene, methyl methacrylate, and acrylonitrile) have been compared[31]. The authors obtained the empirical relation $\lg(k_{1,2}/k_{1,3}) = -0.188e_1 + 1.14$, which is in good agreement with the rearranged Alfrey-Price equations $\lg(k_{1,2}/k_{1,3}) = \lg(Q_2/Q_3) - (e_2 - e_3)e_1$. The differences between the polar and resonance factors for alkyl vinyl sulphides and ethyl vinyl ether were determined from the latter expression:

$$e_2 - e_3 = 0.43; \quad Q_2/Q_3 = 13.8.$$

The nature of the second substituent in vinyl sulphides does not influence significantly either their polymerisation or the degree of their involvement in copolymerisation[31,43]. However, it has been noted that, in the copolymerisation with styrene, phenyl vinyl sulphide is somewhat more reactive than alkyl vinyl sulphides and in homopolymerisation the rate of reaction decreases for $R = CH_2CH_2OH$ and particularly for R=  . B. On the other hand it has been stated[53] that vinylthiobenzothiazole polymerises readily in the presence of boron trialkyls or AIBN.

The rate of copolymerisation of vinyl sulphides with other monomers and their capacity for the formation of alternating copolymers increases in the sequence[31] styrene < methyl methacrylate < acrylonitrile, which parallels the sequence of the electron-accepting capacities of the monomers.

Although a spectrophotometric study of the synthesis of alternating copolymers of alkyl vinyl sulphides with acrylonitrile failed to reveal charge-transfer complexes[31] (CTC), the finding that isobutyl vinyl sulphide can copolymerise with acrylonitrile also in the absence of a radical initiator shows that charge-transfer complexes of the contact type can be formed and can be involved at least in the initiation of such copolymerisation.

At the same time the formation of such a complex has been confirmed spectrophotometrically[54] for the copolymerisation of vinyl sulphides with maleic anhydride. The equilibrium constant for its formation has been determined as 0.035 ± 0.007, while the analogous constant for vinyl ethers is 0.027 ± 0.002. This is related to the difference between the ionisation potentials of vinyl sulphides and vinyl ethers.

The copolymerisation of benzyl vinyl sulphide with SO_2 also proceeds with formation of charge-transfer complexes[55]. Copolymers with equal numbers of units were obtained from methyl vinyl sulphide and vinylene carbonate[56]. Attempts to copolymerise vinyl sulphides with phenylacetylene were unsuccessful[57].

Unfortunately the kinetics of the polymerisation of vinyl sulphides have so far been investigated very inadequately. One can mention the study of Tsuda et al.[58], who carried out the homopolymerisation of phenyl vinyl sulphide and calculated the apparent rate constant, the activation energy, and the entropy of reaction. In the course of a study of the copolymerisation of methyl vinyl sulphide with styrene, the propagation rate constant was determined[59] as 240 litre $mole^{-1}$ min^{-1}. Finally Koton and coworkers[60] determined the activation energy for the polymerisation of phenyl *p*-vinylphenyl sulphide, which proved to be 15.5 ± 1.2 kcal $mole^{-1}$.

In the majority of cases the information concerning the polymerisation of vinyl sulphides is descriptive. Thus it has been reported that the optically active (+)-s-butyl *o*-vinylbenzyl sulphide polymerises spontaneously[21]. When the process is carried out in the presence of AIBN, the product is a polymer with a high optical activity, which completely disappears when the polymer is acted upon by Raney nickel.

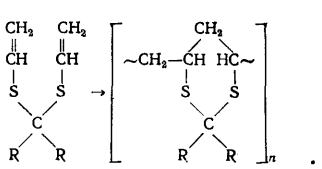
Graft-polymers from amine-containing vinyl sulphides and poly(alkyl acrylates) were obtained by radiation-induced polymerisation[61].

According to patent data, alkoxyalkyl vinyl sulphides readily polymerise and copolymerise with vinyl-containing compounds[62-66], such as derivatives of acrylic acid, vinyl chloride, vinylidene chloride, vinyl, allyl, and methylallyl ethers, and styrene and its derivatives. The polymers and copolymers are capable of being cross-linked[63,66] on heating as a result of transesterification or, in oxidation under mild conditions, as a result of the formation of a disulphide linkage. More vigorous oxidation (aqueous solution of hydrogen peroxide in an acid medium) leads to the formation of sulpho-groups and cation-exchange resins[63,64] which are superior in their ion-exchange properties to the cation exchangers based on polystyrenesulphonic acid[64].

Many patents describe the properties of the polymers and copolymers of vinyl sulphides[22,23,67-69]. It has been stated that thermoplastic polymers[70] with rubberlike properties[71-74], which are suitable for the formation of films and auxiliary materials in the textile industry, can be obtained on the basis of vinyl sulphides. Elastomers[75] with exceptional stability at high temperatures are formed in the copolymerisation of alkyl vinyl sulphides with ethylene in the presence of a small amount of allyl acrylate employed as the vulcaniser. Rubberlike copolymers have been obtained from butadiene and divinyl sulphide by copolymerisation in an emulsion[73]. The same sulphides are recommended as additives to styrene in order to improve the dielectric properties of polystyrene in relation to high-frequency currents[76].

It has been noted[77] that poly(alkyl vinyl sulphides) have higher glass points than the corresponding poly(alkyl vinyl ethers), which is due to the greater density of cohesion energy in the former.

More complex derivatives of the vinyl sulphide series (divinylmercaptals and divinylmercaptols), obtained by the dehydrochlorination of the corresponding bis-(β-chloroethyl)mercaptals and bis-(β-chloroethyl)mercaptoles, polymerise with formation of rubberlike polymers[78]. The polymerisation of the above monomers is carried out in the presence of AIBN (0.1–2 mole %) at 60–80°C both in bulk and in solution. The study of the properties of these polymers showed that the polymerisation proceeds mainly via an intermolecular–intramolecular mechanism with formation of rings in the chain, as in the radical polymerisation of divinylacetals[79]:



Depending on the conditions, linear or cross-linked polymers are obtained[80]. Polymerisation in solution and a low degree of conversion favour the formation of a linear polydivinylmercaptal containing cyclic units in the main chain and soluble in chloroform, benzene, and tetrahydrofuran (THF). Divinylthioacetal, divinylthiobutyral, and the divinylthioketal of acetone cyclopolymerise under the influence of AIBN,[81] forming soluble rubberlike polymers with $[\eta] = 0.1-0.2$. Under analogous conditions, divinylthioformal gives rise to a cross-linked polymer.

The polymerisation of a series of formaldehyde *S*-vinyl mercaptals under the influence of various initiators was investigated by Ringsdorf and coworkers[82]. In contrast to benzoyl peroxide, AIBN leads to polymers with M = 27 000. In the presence of cationic catalysts, only small amounts of oligomers are obtained (owing to the formation of sulphonium ions).

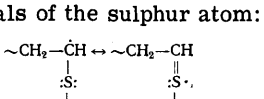
2. Polymerisation of Vinyl Thioacylates

The polymers synthesised on the basis of vinyl thioacylates have aroused considerable interest primarily because they can be used to prepare high-molecular-weight products containing mercapto-groups. The combination of the mercapto-group with a macromolecular structure leads to substances which are important in practice. Such polymers have been suggested as specific ion exchangers and protective agents against radiation[83,84] and also as model compounds for the elucidation of the role of the mercapto-group in certain enzymes[85]. The synthesis of the above polymers by the direct polymerisation of vinylmercaptans presents considerable difficulties owing to the low availability of the latter. Nevertheless, hydrolysis of polymers of vinyl thioacetate, preferably with a 10% NaOH solution in methanol, leads to the formation of polymers containing free mercapto-groups[86]. Polymeric protecting agents against radiation have been obtained by treating with hydrazine hydrate copolymers of vinyl thioacetate with *N*-vinylsuccinimide and *N*-vinylphthalimide[87]. However, these copolymers proved to be very unstable and were readily oxidised on standing in air, yielding insoluble strongly swelling products. The study of the kinetics of the oxidation of polyvinylmercaptan and its model low-molecular-weight analogues with molecular oxygen in various aprotic solvents in the presence of iron sulphate showed[88,89] that the rate of the reaction involving polyvinylmercaptan is more than ten times faster than that involving pentane-1,5-dithiol. For this reason, polythiols are used as cross-linking agents[86]. In most cases the oxidation of polythiols leads to the synthesis of insoluble polymers as a result of the formation of intermolecular disulphide bridges, but, depending on the oxidant, other derivatives can also be obtained. Thus, when stronger oxidising agents (for example HNO_3) were employed, polysulphonic acids were isolated[90].

Water-soluble copolymers containing mercapto-groups have been synthesised from *p*-vinylphenyl thioacetate[91,92]. The polymerisation and copolymerisation have been carried out under the influence of radical initiators. The solubility of the polymers decreased markedly on acidification.

The polymerisation of vinyl thioacetate has been investigated in greater detail[87,93]. It was established that the monomer polymerises fairly readily in the presence of AIBN and copolymerises under these conditions with *N*-vinylsuccinimide, *N*-vinylphthalimide, and *N*-vinylcarbazole. The polymerisation kinetics are characterised by a constant for chain transfer to the vinyl thioacetate molecule $C_M = 0.056$ at 60°C. For comparison Table 2 presents the constants for chain transfer by the monomer for certain vinyl esters.

The authors explained the observed phenomenon by the stabilisation of the radical centre as a result of the involvement of the *d* orbitals of the sulphur atom:



This is in full agreement with spectroscopic data and the chemical behaviour of vinyl thioacetate in free-radical addition reactions[98].

When the reactivities of vinyl acetate ($Q = 0.028$; $e = -0.30$) and vinyl thioacetate ($Q = 1.67$; $e = -1.34$) in

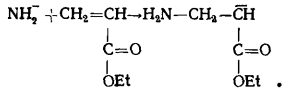
copolymerisation with *N*-vinylsuccinimde were compared, it was found that the replacement of oxygen by sulphur greatly enhances the reactivity of the monomer in copolymerisation.

Table 2. Constants for chain transfer by the monomer (C_M) for certain vinyl esters.

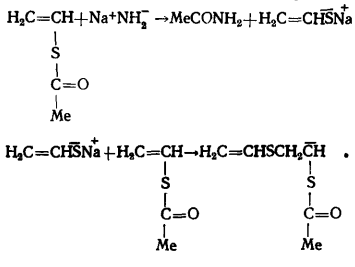
Monomer	Temp., °C	$10^3 C_M$	References
Vinyl acetate	60	0.15	94
Vinyl pelargonate	60	1.5	94
Vinyl stearate	60	2.3	94
Vinyl benzoate	79.6	0.7	95
Vinyl salicylate	70	8.0	96
Allyl acetate	70	0.723	97

Vinyl thioacetate copolymerises with methyl methacrylate [99], vinylene carbonate [100], diethyl maleate [101], maleic anhydride, and diethyl and dimethyl fumarates [102]. The products of the hydrolysis of the copolymers of vinyl thioloacetate and diethyl maleate can be used as cation-exchange resins and bases for coatings. After treatment with concentrated KOH solution in methanol, the copolymers of vinyl thioacetate and ethylene are converted into elastic materials which do not burn even at 250°C. [103,104]

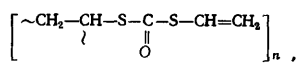
Liquid polymers of vinyl thioacetate have been obtained by its polymerisation with sodium in liquid ammonia [105]. According to elemental analysis and infrared spectra, under these conditions the polymers underwent ammonolysis and contained disulphide rings. The polymers have been used as protective agents against radiation. The polymerisation of vinyl thioacetate was investigated in greater detail by Leonard et al. [106] who showed that, in the polymerisation of vinyl thioacetate under the influence of sodium in liquid ammonia, polymers containing intramolecular and intermolecular disulphide bridges and mercapto-groups are formed, while thioacetate groups are completely absent (as a result of ammonolysis). It was established by elemental analysis that the polymers formed contain less than one amide group per polymer chain, which distinguished them from methacrylonitrile, methyl acrylate, ethyl acrylate, and n-propyl acrylate polymers for which initiation under these conditions takes place with participation of the amide anion [107,108]:



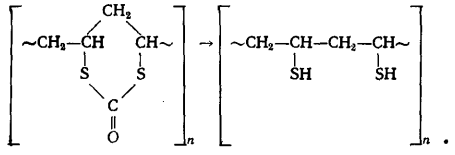
Moreover, a considerable amount of acetamide is formed as a side product in the polymerisation of vinyl thioacetate. On this basis, the author suggested the following mechanism for initiation of the polymerisation [106]:



Depending on the conditions, the *SS'*-divinyl ester of dithiocarbonic acid $(H_2C{=}CH{-}S{-})_2C{=}O$ forms a mixture of soluble and insoluble polymers [109], the soluble part consisting mainly of a polymer with *S*-vinyl thiocarbonate side chains:



If the polymerisation proceeds via an intramolecular-intermolecular mechanism, a soluble polymer containing trimethylene dithiocarbonate rings linked by methylene bridges is formed. These polymers can be converted into polyethylenethiols by subsequent alkaline hydrolysis:



III. POLYMERISATION AND COPOLYMERISATION OF VINYL MONOMERS CONTAINING OXIDISED SULPHUR

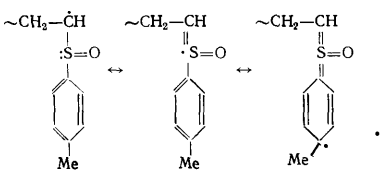
In contrast to α-vinyl sulphides, the double bond in α-vinyl sulphones and sulphoxides is highly activated in relation to nucleophilic reagents [6]. On the other hand, free-radical addition reactions are not very characteristic of such compounds. For example, thiols hardly react with vinyl sulphones on prolonged standing in air; in the presence of AIBN and on heating, a very slow reaction is observed [110]. The lower tendency of αβ-unsaturated sulphones to undergo homolytic addition reactions is explained by the fact that the sulphonyl group is incapable of stabilising adequately the free-radical state [34].

Numerous studies have been made on the structures of the sulphoxide and sulphone groups, the majority of which have been analysed in reviews [111-113]. Despite some conflict among the data obtained using different physical and chemical methods, one can regard it as proved that in the sulphone and sulphoxide groups there are linkages between sulphur and oxygen approaching in their properties a double bond. The *d* orbitals of the sulphur atom play a significant role in these linkages; the linkages are not of the "pure" semipolar type as has been suggested [36,114,115]. There is of course no complete analogy between these multiple bonds and the C=O bond of the keto-group. Firstly the S=O bonds are formed by atoms with much greater electronegativity differences than those between C and O, which enhances their polarity. Secondly these are $p_\pi - d_\pi$ bonds, in contrast to the $p_\pi - p_\pi$ double bonds. Therefore the problem of the conjugation of these bonds with unsaturated systems is also more complex. Nevertheless, the majority of investigators believe that conjugation with a sulphonyl group does not involve the S=O bonds but is limited to the involvement of the *d* shell of the sulphur atom. Examination of the polymerisation of these compounds leads to the same conclusion.

1. Synthesis of Polymers Containing Sulphoxide Groups

Polymers containing sulphoxide groups should in principle possess a set of interesting properties characteristic of their low-molecular-weight analogues, which serve as extracting agents for metals [116] and flotation

agents [117], and behave as physiologically active substances [118]. However, until recently these polymers were not obtained by the direct polymerisation of vinyl sulphoxides. It was believed [3] that the sulphoxide group inhibits both radical and ionic polymerisation. Indeed it was noted that methyl vinyl sulphoxide does not undergo homopolymerisation in the presence of radical initiators [119]. However it does copolymerise with styrene and methyl methacrylate giving low yields of copolymers with a low content of sulphoxide groups. Nevertheless, this was sufficient to determine the copolymerisation parameters and to calculate $Q = 0.10$ and $e = 0.9$. The low value of the resonance stabilisation factor compared with, for example, methyl vinyl sulphide [34] ($Q = 0.35$), led to the conclusion that there is no conjugation between the vinyl and sulphoxide groups or such conjugation is very weak. On the other hand, in the copolymerisation of the optically active *p*-tolyl vinyl sulphoxide (M_1) with styrene (M_2) a higher value of r_1 ($r_1 = 0.1 \pm 0.07$; $r_2 = 5.77 \pm 0.10$) was found [120] than for methyl vinyl sulphoxide (M_1) in its copolymerisation with the same monomer ($r_1 = 0.01$; $r_2 = 4.2$). This is probably related to the additional possibility of the delocalisation of the unpaired electron:



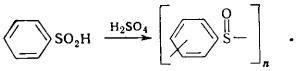
Polymers containing sulphoxide groups have been obtained by an indirect method†: by the polycondensation of sulphoxide-containing bifunctional compounds and by the oxidation of polythioethers or the products of the reaction of mercaptans with rubbers. Thus a sulphoxide-containing polycarbonate with a melting point of 230–250°C was obtained [121] by the reaction of phosgene with bis-(4-hydroxyphenyl) sulphoxide. The polycarbonate [122] based on bis-(4-hydroxy-3-methylphenyl) sulphoxide melts at 190°C.

Poly(phenylene sulphoxides) suitable for the formation of fibres, films, and high-temperature adhesives have been obtained [123] by the oxidation of the sulphide bridges in poly(phenylene sulphide) with nitric acid. The polymers are stable above 600°C. Other poly(phenylene sulphoxides) were obtained similarly [124] and were used to prepare, after heat treatment at 350–700°C in argon, thermostable non-combustible polymers [125].

The oxidation of polythietanes with one equivalent of hydrogen peroxide leads to the corresponding sulphoxides [126].

Polymers containing the sulphoxide group in the side chain have been obtained by the oxidation with hydrogen peroxide of the products of the addition of mercaptans to polybutadiene [127]. The authors noted that in all such cases sulphone as well as sulphoxide groups are formed and explained this observation by the different solubilities of the polymer in the course of the oxidation process. However, we showed [128,129] that, even when the medium remains homogeneous in the course of the oxidation of polymeric thioethers, selective oxidation cannot be achieved. The polymer contains sulphone as well as non-oxidised sulphide groups in addition to the sulphoxide groups. Moreover, the non-selectivity of the oxidation is also observed when acetic anhydride is used as a solvent, although it was established previously that monomeric sulphides are oxidised selectively in this medium to the sulphoxides [130,131]. The unusual behaviour in the oxidation of the sulphur atoms in the polymer is probably associated with the conformation of the polymer chain which hinders the approach of the oxidant to certain sulphide groups.

A polymer of the sulphonium type was obtained by the reaction of poly(methyl *p*-vinylphenyl sulphide) with dimethyl sulphate; this can be converted in turn into a sulphoxide polymer by treatment with a mixture of dimethyl sulphoxide and benzaldehyde in the presence of potassium t-butoxide [132]. Finally arenesulphinic acids form polymeric sulphoxides on dissolution in concentrated sulphuric acid [133]. Thus benzenesulphinic acid gives a 50% yield of a solid product which swells in alcohol and was shown subsequently to have the following structure [134]:



Direct polymerisation of vinyl sulphoxides was achieved for the first time by ourselves [129,135]. It was found that, contrary to the existing hypothesis concerning the inhibition of the polymerisation by the sulphoxide group, vinyl sulphoxides undergo homopolymerisation when acted upon by anionic catalysts. Naphthylsodium and the sodium–naphthalene complex were used as such catalysts. The process is fairly rapid and leads to the formation of oligomers ($M \simeq 2000$).

We may note that the rate of polymerisation of ethyl vinyl sulphoxide is somewhat lower than that of the corresponding sulphone, which may be related both to the lower nucleophilicity of the double bond in vinyl sulphoxides [6] and to the reduction of the efficiency of the catalyst in consequence of complex formation involving the sulphoxide group [136].

All attempts to polymerise vinyl sulphoxides under free-radical conditions failed despite the wide variety of initiators and conditions employed [129]. Nevertheless an inhibiting effect of sulphoxide groups is unlikely in this instance. It is sufficient to recall that dimethyl sulphoxide is quite widely used as a solvent in radical polymerisation processes and does not cause the destruction of the radical centres.

2. Polymerisation and Copolymerisation of Vinyl Sulphones

The polymerisation of $\alpha\beta$-unsaturated sulphones has been little investigated hitherto and is largely described in patents. According to these data, the polymers obtained from vinyl sulphones have valuable technical properties [137–141]. Thus the introduction of the sulphone group into the polymer increases its thermal stability and resistance to benzene [142,143]. The copolymers of dialkenyl sulphones [144] are recommended as additives to lubricating oils to improve their viscosity index. Vinyl sulphones are copolymerised with acrylonitrile and vinyl ethers in dimethylformamide [145] in order to obtain very strong thermostable and readily dyed fibres. Copolymers based on isopropenyl sulphones $RSO_2(CH_3)C{=}CH_2$ (R = alkyl, aryl, or alkylaryl) and vinyl acetate, methyl acrylate,

† Although these methods have no direct bearing on the polymerisation of vinyl sulphoxides, nevertheless it is thought necessary to examine them in this review since, as stated above, until recently polymers containing sulphoxide groups were not obtained by direct polymerisation.

styrene, acrylonitrile, and vinyl chloride are recommended for the synthesis of strong sheets, films, and compositions susceptible to mechanical treatment (moulding, extruding)[146]. Materials suitable for the formation of films and protective coatings and distinguished by a satisfactory capacity for being dyed are obtained by the copolymerisation of aromatic vinyl sulphones having the general formula $XC_6H_4(CH_2)_nY(CH_2)_2SO_2CH=CH_2$, where $X = SO_3H$, or SO_2CH_3 and $Y = O$, NH, or NC_2H_5, with acrylonitrile and vinyl chloride[147].

The study of the polymerisation of vinyl sulphones established that, despite their low tendency to undergo free-radical addition reactions, radical polymerisation of ethyl vinyl sulphone is fairly rapid and leads to a quantitative yield of the polymer[129,148]. Moreover, the rate of polymerisation of ethyl vinyl sulphone is higher than that of the corresponding sulphide[128], which may be explained by the absence of conjugation between the sulphenyl and vinyl groups in ethyl vinyl sulphone. This hypothesis had been proved earlier by Price[34,35], who obtained a very low reactivity factor ($Q = 0.07-0.11$) in a study of the copolymerisation of methyl vinyl and phenyl vinyl sulphones with styrene and vinyl acetate, in contrast to the corresponding sulphides ($Q = 0.35$).

At the same time one should note that, although the rate of homopolymerisation of ethyl vinyl sulphone is fairly high, it is possible to obtain only polymers with a low molecular weight. It was established subsequently[129] that the chain transfer constant for ethyl vinyl sulphone ($C_M = 0.087$) is very high, approaching the value of C_M for allyl acetate[97] and allyl chloride[149].

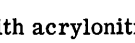
It might have been supposed that this is due to the presence of the mobile α-hydrogen atom, as happens in the polymerisation of various *S*-vinylmethylene disulphones[150,151]. The latter are known to form only oligomers under both free-radical and ionic conditions. This is due to the chain transfer by the active methylene group, the degree of polymerisation falling with increase of the acidity of the CH_2 group.

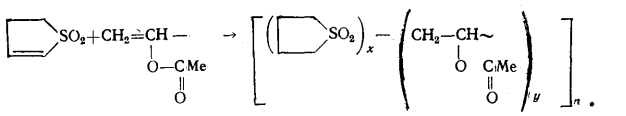
However, a study[129] of the kinetics of the polymerisation of ethyl vinyl sulphone under the influence of benzoyl peroxide showed that not only a high constant for chain transfer to the monomer and independence of the molecular weight of the polymer of initiator concentration but also an approach to unity of the reaction order with respect to the initiator is observed. Moreover, the activation energy for the process proved to be 23.8 kcal mole^{-1}, which is also somewhat high. All these findings indicate the formation of stable radicals in the process.

Stable radicals are probably formed as a result of the involvement of the SO_2 group in the chain transfer reaction. This is demonstrated also by the decrease of the rate of polymerisation in the presence of diethyl and dimethyl sulphones[129].

As expected, the anionic polymerisation of vinyl sulphones proceeds at a high rate, but, as in radical polymerisation, it leads to the formation of only low-molecular-weight products[129]. The low efficiency of the catalysts employed is also striking. In this case intense chain transfer is probably accompanied by the deactivation of the catalyst both as a result of metallation[152] and the formation of a complex via the oxygen atom of the sulphonyl group[153]. The unsuccessful attempts at the polymerisation of ethyl vinyl sulphone under the influence of Ziegler catalysts and boron alkyls[129] can also be evidently explained by the possibility of complex formation.

In the anionic copolymerisation of butyl vinyl sulphone with acrylonitrile a tendency was noted towards the formation of alternating polymers, which the authors attributed to steric effects[154]. $\alpha\beta$-Unsaturated sulphones copolymerise fairly readily with other monomers[155,156].

It has been noted that the copolymerisation of allyl sulphones with vinyl monomers leads to high-molecular-weight products[157]. 3-Sulpholene  does not polymerise at a "moderate" temperature (about 60°C); at an elevated temperature (80–140°C) a copolymer with alternating butadiene and SO_2 units is formed[158,159]. Although 2-sulpholene does not form homopolymers it does copolymerise with vinyl acetate[160]:



The highest sulpholene content in the copolymer does not exceed 50%, and an appreciable decrease of the viscosity of the copolymer is observed with increase of the sulpholene content in the monomer mixture.

Numerous data have been published in patents on the copolymerisation of vinyl sulphones[142-147,161-167]. Thus an interesting method for the preparation of cross-linked sulphone polymers includes the synthesis of oligomers capable of further polymerisation or copolymerisation with vinyl monomers[162]. The oligomers were obtained by the reaction with glycols or primary amines of monosulphones having the general formula $SO_2(CR=CR'R'')_2$ or polysulphones of the type $R'''(SO_2CR=CR'R'')_n$, where R''' is an organic substituent without functional groups whose valency is 2–6, R, R', and R'' = H, alkyl, or aryl. The oligomers are synthesised in the presence of an excess of the monosulphone (divinyl, propenyl vinyl, and ethyl vinyl sulphones) or polysulphone [1,4-bis(vinylsulphonyl)butane, 4,4-bis(vinylsulphonyl)biphenyl, etc.]. The polymerisation and copolymerisation of the oligomers are carried out under the influence of peroxide initiators such as H_2O_2, benzoyl peroxide, etc. Polymers of aminoaryl vinyl sulphones are recommended for the manufacture of polymeric dyes in view of the presence of a fairly large number of amino-groups susceptible to diazotisation[163,164]. Organometallic compounds and alkali metal hydrides or amides are employed as catalysts. Homopolymerisation and copolymerisation are carried out in bulk, in solution, or in a dispersion. The copolymers are suitable for the formation of fibres and also as stabiliser and auxiliary materials in the textile industry[165,166].

Polymeric dyes have also been obtained by the anionic polymerisation and copolymerisation of vinyl sulphones having the general formula $H_2C=CHSO_2ArN=NRNH_2$, where Ar is an aryl radical which can contain ring substituents[167].

It is noteworthy that, under free-radical conditions, vinyl sulphones copolymerise vigorously with inactive monomers, for example with vinyl acetate[34]. At the same time in the copolymerisation of methyl vinyl sulphone (M_1) with styrene (M_2) the percentage of its involvement is very slight ($r_1 = 0.01$; $r_2 = 2.0$).[34] Ethyl vinyl sulphone does not copolymerise with butadiene and behaves under these conditions merely as a diluent i.e. with increase of its concentration in the initial mixture the rate of homopolymerisation of butadiene falls[129].

In conclusion of this section one should note that the polymerisation of vinyl sulphones is fairly rapid both under

free-radical and ionic conditions. At the same time, owing to the specific features of the sulphone group, this entails the formation of only low-molecular-weight products, because of the intense chain transfer to the monomer. The polymerisation process is also complicated by side reactions leading to a decrease of the efficiency of the catalysts: interaction of the radical centre with the SO_2 group and metallation or complex formation involving the sulphone group in polymerisation under the influence of anionic catalysts.

The data presented above show that, despite the large number of studies on the polymerisation of unsaturated sulphur-containing compounds, there have been only a limited number of kinetic investigations. This hinders appreciably the interpretation of the results. Much still remains to be done in the field of the polymerisation of this interesting class of compounds.

REFERENCES

1. J. Lal, in "The Chemistry of Cationic Polymerisation" (Edited by P. A. Plesch) (Translated into Russian), Izd. Mir, Moscow, 1966, p. 402.
2. A. A. Sakharova, Symposium, "Uspekhi v Oblasti Sinteza Elementoorganicheskikh Polimerov" (Advances in the Synthesis of Polymers Derived from Organic Derivatives of the Elements (Edited by V. V. Korshak), Izd. Nauka, Moscow, 1966, p. 173.
3. E. J. Goethals, J. Macromol. Sci., C2, 73 (1968).
4. C. E. Meyer et al., Rubber World, 136, 529, 625 (1957).
5. Chem. Eng., 66, 40 (1959).
6. E. N. Prilezhaeva, Doctoral Thesis, Institute of Organic Derivatives of the Elements, USSR Academy of Sciences, Moscow, 1963.
7. U. S. P. 2 125 649 (1938); Chem. Abs., 32, 7615 (1938).
8. B. P. 445 434 (1936); Chem. Abs., 30, 6858 (1936).
9. French P. 794 022 (1936); Chem. Abs., 30, 4594 (1936).
10. W. Reppe et al., Annalen, 601, 81 (1956).
11. U. S. P. 2 769 802 (1956); Chem. Abs., 51, 6220 (1957).
12. U. S. P. 2 462 703 (1949); Chem. Abs., 43, 3660 (1949).
13. U. S. P. 2 691 646 (1954); Chem. Abs., 49, 2118 (1955).
14. M. F. Shostakovskii, E. N. Prilezhaeva, and N. I. Uvarova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 526 (1954).
15. M. F. Shostakovskii, E. N. Prilezhaeva, and V. M. Karavaeva, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk (1957).
16. M. F. Shostakovskii, E. N. Prilezhaeva, and V. M. Karavaeva, Vysokomol. Soed., 1, 582 (1959).
17. M. F. Shostakovskii and E. N. Prilezhaeva, Vysokomol. Soed., 1, 594 (1959).
18. M. F. Shostakovskii, E. N. Prilezhaeva, and V. M. Karavaeva, Izv. Vys. Ucheb. Zaved., Khim. i Khim. Tekhnol., 2, 761 (1959).
19. M. F. Shostakovskii, "Prostye Vinilovye Efiry" (Vinyl Ethers), Izd. Akad. Nauk SSSR, Moscow, 1952.
20. G. Baddeley, J. Chem. Soc., 663 (1950).
21. C. G. Overberger and L. C. Palmer, J. Amer. Chem. Soc., 78, 666 (1956).
22. B. P. 837 802 (1960); Chem. Abs., 55, 2197 (1961).
23. U. S. P. 2 636 022 (1953); Chem. Abs., 47, 7826 (1953).
24. U. S. P. 2 522 502 (1950); Chem. Abs., 45, 2903 (1951).
25. U. S. P. 2 947 730 (1960); Chem. Abs., 54, 26 010 (1960).
26. Dutch P. 6 413 745 (1965); Chem. Abs., 63, 18 302 (1965).
27. M. F. Shostakovskii, E. N. Prilezhaeva, and V. M. Karavaeva, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1250 (1958).
28. M. F. Shostakovskii, E. N. Prilezhaeva, and N. I. Uvarova, Soobshch. Nauch. Rabot. Chl. Vses. Khim. im. Mendeleeva, No. 3, 21 (1955).
29. M. F. Shostakovskii and V. A. Gladyshevskaya, Soobshch. Nauch. Rabot. Chl. Vses. Khim. im. Mendeleeva, No. 3, 25 (1955).
30. M. F. Shostakovskii, E. N. Prilezhaeva, N. A. Gershtein, and V. M. Karavaeva, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 904 (1959).
31. T. Otsu and H. Inoue, J. Macromol. Sci., A-4, 35 (1970).
32. W. Tagaki, T. Tada, R. Nomura, and S. Oae, Bull. Chem. Soc. Japan, 41, 1696 (1968).
33. C. E. Scott and C. C. Price, J. Amer. Chem. Soc., 81, 2672 (1959).
34. C. C. Price and J. Zomlefer, J. Amer. Chem. Soc., 72, 14 (1950).
35. C. C. Price and H. Morita, J. Amer. Chem. Soc., 75, 4747 (1953).
36. C. C. Price and R. G. Gillis, J. Amer. Chem. Soc., 75, 4750 (1953).
37. E. D. Holly, J. Polymer Sci., 36, 329 (1959).
38. U. S. P. 2 832 806 (1958); Chem. Abs., 52, 14 682 (1958).
39. M. F. Shostakovskii, E. N. Prilezhaeva, and V. M. Karavaeva, Vysokomol. Soed., 1, 781 (1959).
40. K. Tsuda, S. Kobayashi, and T. Otsu, J. Polymer Sci., A-1, 6, 41 (1968).
41. M. Imoto, M. Kinoshita, and N. Nishigaki, Makromol. Chem., 94, 238 (1966).
42. M. F. Shostakovskii, E. N. Prilezhaeva, and A. M. Khomutov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1230 (1956).
43. V. M. Karavaeva, E. N. Prilezhaeva, and M. F. Shostakovskii, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 650 (1957).
44. M. F. Shostakovskii and E. N. Prilezhaeva, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 517 (1954).
45. M. F. Shostakovskii, E. N. Prilezhaeva, and M. I. Uvarova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1245 (1958).
46. U. S. P. 2 528 455 (1950); Chem. Abs., 45, 1814 (1951).
47. U. S. P. 2 514 185 (1950); Chem. Abs., 44, 11 167 (1950).
48. J. B. Kinsinger, J. R. Panchak, et al., J. Appl. Polymer Sci., 9, 429 (1965).
49. J. C. H. Hwa and L. Miller, J. Polymer Sci., 55, 197 (1961).
50. M. F. Shostakovskii, F. P. Sidel'kovskaya, M. G. Zelenskaya, and E. S. Morgunova, see Ref. 28, p. 5.
51. T. Alfrey, J. Bohrer, and H. F. Mark, "Copolymerization" (Translated into Russian), Inostr. Lit., Moscow, 1953.

52. R. H. Wiley and G. L. Mayberry, J. Polymer Sci., A-1, 217 (1963).
53. R. Y. Kern, J. Polymer Sci., 43, 549 (1960).
54. T. Otsu and H. Inoue, Makromol. Chem., 128, 31 (1969).
55. C. G. Overberger and J. A. Moore, Chem. Ind. (London), 24 (1968).
56. J. M. Judge and C. C. Price, J. Polymer Sci., 41, 435 (1959).
57. C. C. Price and C. E. Greene, J. Polymer Sci., 6, 111 (1951).
58. K. Tsuda, S. Kobayashi, and T. Otsu, J. Macromol. Sci., A-1, 6, 1025 (1967).
59. H. W. Melwille and G. M. Burnett, J. Polymer Sci., 13, 417 (1957).
60. P. A. El'tsova, M. M. Koton, O. K. Mineeva, and O. K. Surnina, Vysokomol. Soed., 1, 1369 (1959).
61. U. S. P. 2 296 126 (1960); Chem. Abs., 55, 14 996 (1961).
62. B. P. 826 659 (1960); Chem. Abs., 54, 16 010 (1960).
63. U. S. P. 2 906 741 (1959); Chem. Abs., 54, 2811 (1960).
64. U. S. P. 2 868 738 (1959); Chem. Abs., 53, 7465 (1959).
65. BRD P. 1 061 077 (1959); Chem. Abs., 55, 20 512 (1961).
66. J. C. H. Hwa, J. Amer. Chem. Soc., 81, 3604 (1959).
67. U. S. P. 3 326 867 (1967); Chem. Abs., 67, 53 676 (1967).
68. U. S. P. 2 996 484 (1961); Chem. Abs., 55, 27 987 (1961).
69. U. S. P. 3 206 400 (1965); Chem. Abs., 63, 12 953 (1965).
70. U. S. P. 2 877 214 (1959); Chem. Abs., 53, 11 891 (1959).
71. U. S. P. 2 605 256 (1952); Chem. Abs., 46, 10 688 (1952).
72. BRD P. 888 768 (1953); Chem. Abs., 51, 2327 (1957).
73. B. P. 562 269 (1944); Chem. Abs., 40, 492 (1946).
74. U. S. P. 3 048 569 (1960).
75. B. P. 965 625 (1964); Chem. Abs., 61, 14 876 (1964).
76. A. V. Hippei and L. C. Wescon, Ind. Eng. Chem., 38, 1121 (1946).
77. J. Lal and G. S. Trick, J. Polymer Sci., A-2, 4559 (1964).
78. S. G. Matsoyan and A. A. Saakyan, Vysokomol. Soed., 3, 1755 (1961).
79. S. G. Matsoyan, "Mezadunarodnyi Sympozium po Makromolekulyarnoi Khimii, SSSR, Moskva, 1960" (International Symposium on Macromolecular Chemistry, Moscow, USSR, 1960), Section 1, p.101.
80. H. Ringsdorf and C. G. Overberger, J. Polymer Sci., 61, S11 (1962).
81. S. G. Matsoyan and A. A. Saakyan, Izv. Akad. Nauk Arm. SSR, Otd. Khim. Nauk, 463 (1962).
82. K. D. Gollmer, F. H. Muller, and H. Ringsdorf, Makromol. Chem., 92, 122 (1966).
83. H. G. Cassidy, J. Amer. Chem. Soc., 71, 402 (1949).
84. K. A. Kun, J. Polymer Sci., A-1, 4, 847 (1966).
85. E. S. G. Barron, Adv. Enzymol., 11, 219 (1951).
86. U. S. P. 2 378 535 (1945); Chem. Abs., 39, 4331 (1945).
87. G. Hardy, J. Varga, K. Nyitray, I. Czajlik, and L. Zubonyai, Vysokomol. Soed., 4, 758 (1964).
88. C. G. Overberger, K. H. Burg, and W. H. Daly, J. Amer. Chem. Soc., 87, 4125 (1965).
89. V. G. Overberger, J. K. Ferraro, and F. W. Ortung, J. Org. Chem., 26, 3458 (1961).
90. B. P. 568 565 (1945); Chem. Abs., 41, 4509 (1947).
91. C. G. Overberger and A. Lebobits, J. Amer. Chem. Soc., 77, 3675 (1955).
92. C. G. Overberger and A. Lebobits, J. Amer. Chem. Soc., 78, 4792 (1956).
93. K. Furukawa, M. Nomura, and R. Oda, Bull. Inst. Chem. Research. Kyoto Univ., 28, 74 (1952).
94. C. F. Thomson, W. S. Post, and L. P. Witnauer, J. Amer. Chem. Soc., 81, 2552 (1959).
95. S. Benerjee and M. S. Muthana, J. Polymer Sci., 37, 469 (1959).
96. G. Hardy, V. Spiegel, and K. Nyitray, Vysokomol. Soed, 3, 144 (1961).
97. A. A. Vainsheidt and G. Hardy, Acta Chem. Acad. Sci. Hung., 20, 381 (1959).
98. N. P. Petukhova and E. N. Prilezhaeva, Zhur. Org. Khim., 2, 1947 (1966).
99. C. G. Overberger and J. J. Ferraro, J. Org. Chem., 27, 3539 (1962).
100. C. G. Overberger, H. Biletch, and R. G. Nickerson, J. Polymer Sci., 27, 381 (1958).
101. U. S. P. 2 418 426 (1947); Chem. Abs., 41, 4011 (1947).
102. B. P. 585 755 (1947); Chem. Abs., 42, 2987 (1948).
103. U. S. P. 2 377 753 (1945); Chem. Abs., 39, 3702 (1945).
104. B. P. 585 396 (1947); Chem. Abs., 41, 4006 (1947).
105. U. S. P. 283 536 (1962); Chem. Abs., 60, 5647 (1964).
106. F. Leonard, G. A. Hanks, and R. K. Kulkarni, J. Polymer Sci., A-1, 4, 449 (1966).
107. C. G. Overberger, H. Yuki, and N. Urakawa, J. Polymer Sci., 45, 127 (1960).
108. F. Leonard, A. J. Szlachtun, and I. Cort, J. Polymer Sci., 9, 339 (1953).
109. H. Ringsdorf and C. G. Overberger, Makromol. Chem., 44, 418 (1961).
110. M. F. Shostakovskii, E. N. Prilezhaeva, L. V. Tsymbal, R. Ya. Tolchinskaya, and N. G. Starova, Zhur. Obshch. Khim., 31, 2496 (1961).
111. Yu. A. Kolesnik and V. V. Kozlov, Uspekhi Khim., 37, 1192 (1968) [Russ. Chem. Rev., No. 7 (1968)].
112. J. Strating, in "The Chemistry of Organic Sulphur Compounds" (Edited by N. Kharasch), London–New York–Oxford–Paris, Pergamon Press, 1961, p. 146.
113. C. M. Suter, "Chemistry of Organic Sulphur Compounds" (Translated into Russian), Inostr. Lit., Moscow, 1950.
114. A. I. Vogel, J. Chem. Soc., 1820 (1948).
115. A. I. Vogel et al., J. Chem. Soc., 514 (1952).
116. G. Laurance, Compt. rend., 269, 352 (1969).
117. I. U. Numanov, G. D. Gal'pern, E. N. Karaulova, N. N. Bezinger, V, P. Chaiko, A. I. Skobelina, and G. V. Speshilova, Izv. Akad. Nauk Turkmen. SSR, Ser. Fiz., Tekh., Khim. i Geol., 6, 31 (1963).
118. U. S. P. 2 654 667 (1953); Chem. Abs., 48, 1621 (1954).
119. C. C. Price and R. D. Gilbert, J. Amer. Chem. Soc., 74, 2073 (1952).
120. J. E. Mulvaney and R. A. Ottaviani, J. Polymer Sci., A-1, 8, 2293 (1970).
121. BRD P. 1 047 430 (1958); Chem. Abs., 55, 4046 (1961).
122. H. Schell, Ind. Eng. Chem., 51, 157 (1959).
123. U. S. P. 3 326 865 (1963).

124. Belg. P. 644 780 (1964); Chem. Abs., 63, 7182 (1965).
125. Belg. P. 644 106 (1964); Chem. Abs., 63, 5841 (1965).
126. C. C. Price and E. A. Blair, J. Polymer Sci., A-1, 5, 171 (1967).
127. G. E. Meyer, in "Chemistry of Sulphides (Edited by A. V. Tobolsky), Interscience Publ., 1968, p. 113.
128. A. V. Sviridova and E. N. Prilezhaeva, Vysokomol. Soed., A9, 1335 (1967).
129. A. V. Sviridova, Candidate's Thesis, Institute of General Chemistry, USSR Academy of Sciences, Moscow, 1971.
130. E. N. Prilezhaeva, A. V. Sviridova, V. I. Laba, and G. A. Azymova, USSR P. 314 752 (1970); Byul. Izobret., No. 28 (1971).
131. A. V. Sviridova, V. I. Laba, and E. N. Prilezhaeva, Zhur. Org. Khim., 7, 2480 (1971).
132. Shigeo Tanimoto, Jiro Horikawa, and Ryohei Oda, J. Synth. Org. Chem. Japan, 27, 989 (1969).
133. T. P. Hilditch, J. Chem. Soc., 97, 2579 (1910).
134. Toyo Soda Manufacturing Co. Ltd., Japan, 17, 773 (1965).
135. A. V. Sviridova and E. N. Prilezhaeva, USSR P. 226 150 (1966); Byul. Izobret., No. 28 (1968).
136. F. A. Cotton and R. Francis, J. Amer. Chem. Soc., 82, 2986 (1960).
137. U. S. P. 2 507 147 (1950); Chem. Abs., 45, 3861 (1951).
138. R. H. Wiley and J. M. Schmitt, J. Amer. Chem. Soc., 78, 2169 (1956).
139. R. H. Wiley and J. M. Schmitt, J. Polymer Sci., 27, 587 (1958).
140. U. S. P. 3 476 715 (1969); Chem. Abs., 72, 13 202 (1970).
141. U. S. P. 3 247 133 (1966); Chem. Abs., 64, 19 918 (1966).
142. U. S. P. 2 472 672 (1949); Chem. Abs., 43, 7266 (1949).
143. U. S. P. 2 538 100 (1951); Chem. Abs., 45, 3653 (1951).
144. U. S. P. 3 244 676 (1960).
145. BRD. P. 937 616 (1956); Chem. Abs., 52, 21 249 (1958).
146. U. S. P. 2 843 570 (1958); Chem. Abs., 52, 17 797 (1958).
147. U. S. P. 3 235 535 (1966); Chem. Abs., 64, 17 490 (1966).
148. M. F. Shostakovskii, E. N. Prilezhaeva, and A. V. Sviridova, Dokl. Akad. Nauk SSSR, 146, 837 (1962).
149. P. D. Bartlett and R. Altshul, J. Amer. Chem. Soc., 67, 812, 816 (1945).
150. H. Diefenbach, F. H. Müller, and H. Ringsdorf, Kolloid Z., 203, 158 (1965).
151. H. Diefenbach and F. H. Müller, Kolloid Z., 209, 141 (1966).
152. R. G. Karpenko, Candidate's Thesis, Institute of General Chemistry, USSR Academy of Sciences, Moscow, 1970.
153. V. V. Puchkova, E. N. Gur'yanova, R. R. Shifrina, and K. A. Kocheshkov, Dokl. Akad. Nauk SSSR, 207, 886 (1972).
154. F. C. Foster, J. Amer. Chem. Soc., 74, 2299 (1952).
155. U. S. P. 3 499 073 (1970); Chem. Abs., 72, 122 794 (1970).
156. BRD. P. 1 064 720 (1959); Chem. Abs., 55, 7919 (1961).
157. BRD. P. 878 718 (1953); Chem. Abs., 51, 1656 (1957).
158. Y. Minoura and S. Nakajima, J. Polymer Sci., A-1, 4, 2929 (1966).
159. E. J. Goethals, Makromol. Chem., 109, 132 (1967).
160. J. E. Herz and V. Stannet, J. Polymer Sci., B, 4, 995 (1966).
161. U. S. P. 2 475 424 (1949); Chem. Abs., 43, 8211 (1949).
162. U. S. P. 3 153 021 (1960).
163. BRD. P. 1 129 697 (1962).
164. BRD. P. 1 163 548 (1961).
165. Belg. P. 612 398 (1962); Chem. Abs., 58, 1559 (1963).
166. BRD. P. 1 168 639 (1961).
167. BRD. P. 1 173 652 (1964); Chem. Abs., 61, 13494 (1964).

Zelinskii Institute of
Organic Chemistry,
USSR Academy of
Sciences, Moscow